THERMODYNAMIC SIMULATION OF SLAG SYSTEMS CONCERNING THE PRODUCTION OF STAINLESS STEELS[1]

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Abstract

Slags may be studied and used under greatly different conditions, from that of atmospheric air to the strongly reducing conditions of smelting furnaces. For chromium containing slags, changes in oxygen pressure noticeably affect its composition, because of the multivalence state of chromium ions in slags. Aim of the current paper is to evaluate the influence of the oxygen pressure in the behavior of chromium containing slags. This influence was determined with the assistance of the *FactSage* software (version 5.5) and databases from the FACT group. Slags of two compositions were studied in this work: $CaO-CrO-Cr_2O_3$ and $CaO-SiO_2-CrO-Cr_2O_3$, (with N CaO / N SiO_2 = 1). For each of them, two conditions were specially interesting: metallic chromium saturated slags and chromium oxide saturated slags.

Key words: Slags; Stainless steel; Computational thermodynamics

SIMULAÇÃO TERMODINÂMICA DE SISTEMAS DE ESCÓRIAS LIGADAS À PRODUÇÃO DE AÇOS INOXIDÁVEIS

Resumo

Escórias podem ser estudadas e utilizadas sob condições muito diferentes, desde aquela ao ar, até as fortemente redutoras, utilizadas em fornos para redução de minérios. Para escórias contendo cromo, alterações na pressão de oxigênio afetam sensivelmente a sua composição, por causa do estado multivalente dos íons de cromo nas escórias. O objetivo deste trabalho é avaliar a influência da pressão de oxigênio no comportamento de cromo contido nas escórias. Essa influência foi determinada com o auxílio do software FactSage (versão 5.5) e dos bancos de dados do grupo FACT. Escórias de duas composições foram estudadas neste trabalho: $CaO-CrO-Cr_2O_3$ e $CaO-SiO_2-CrO-Cr_2O_3$, (com CaO N / N SiO_2 = 1). Para cada uma delas, duas condições foram especialmente interessantes: escórias saturadas com cromo metálico e escórias saturadas com óxido de cromo.

Palavras-chave: Escórias; Aços inoxidáveis; Termodinâmica computacional.

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1 INTRODUCTION

Slags are the liquid solutions consisting mainly of molten metal oxides and silicates that float on the top of molten metals, including iron and steels. The importance of slags for the iron and steelmaking industry is deeply revealed by the straight proverb: 'Take care of the slag and the steel will take care of itself'.(1)

Actually, not all substances floating on the melt are liquid but, regardless of the physical state, the word still applies. A partially liquid slag consists of one or more solid minerals (silicates, oxides, carbides, sulfides, etc.) 'mixed' with the liquid. From the metallurgical thermodynamics point of view, it is important to recognize that either the liquid as well as each one of the other solid minerals (compounds and solid *solutions*) are classified as *phases*.

As pointed out by Rosenqvist,(2) slags may be studied and used under greatly different conditions, from that of atmospheric air to the strongly reducing conditions of smelting furnaces. For slags consisting only of "white" oxides SiO_2, Al_2O_3, CaO, and MgO these changes in oxygen pressure do *not* noticeably affect the composition of the slag. This attribute can be primarily related to the absence of oxides of different valencies in these metal-oxide systems. For slags containing manganese, chromium, titanium, and iron oxides, however, considerable changes may occur.

Displays of stable phase fields as a function of some selected state variables (*e.g.* temperature, composition) may be affected by the system pressure. This is the case for Cr-containing molten slags systems, because of the multivalence state of chromium ions in slags.(3) For this metal, several oxidation states are possible: Cr^{2+}, Cr^{3+}, Cr^{6+}, and probably Cr^{4+} and Cr^{5+} as well.(4)

Liquidus-phase relations in the system CaO-chromium oxide-SiO_2 have been determined previously in air and under strongly reducing conditions. In air, the chromium is present predominantly in the trivalent state (Cr^{+3}), whereas under reducing conditions most of the chromium is present in the divalent state (Cr^{+2}). The lowering of pO_2 (which corresponds to reducing the chromium from Cr^{3+} to Cr^{2+}) cause a dramatic decrease in liquidus and solidus temperatures and a significant increase in the solubility of chromium oxide in the liquid phase.(5)

According to Villiers and Muan,(4) the strongly reducing conditions can be imposed either by equilibrating the oxide phases with a metal phase (*e.g.* Cr) or by using appropriate gas mixtures (*e.g.*, CO_2-H_2).

In addition, these authors state that the major parts of the system CaO-chromium oxide-SiO_2 in air (mixtures of compositions on the SiO_2 side of the join Ca_2SiO_4-$CaCr_2O_4$) may be considered ternary, because essentially all the chromium is present as Cr^{3+}. In the more basic part of the system (mixtures of compositions on the CaO side of the join Ca_2SiO_4-$CaCr_2O_4$), however, appreciable amounts of the chromium are present in higher oxidation states (probably mainly as Cr^{6+}).(4)

To conclude, all the considerations presented in the following investigation will be limited to the equilibrium aspects of the systems, in spite of the recognition that kinetic aspects may be equally important. The thermodynamic approach does, however, establish the direction of the reactions and the limiting conditions.

2 SOFTWARE AND THERMODYNAMIC DATA

The software employed in the present work is the *FactSage* (version 5.5), described by Bale et al.(6) This software contains the *Equilib* module, which is the Gibbs energy minimization workhorse of *FactSage.* It calculates the concentrations of chemical species at the state of equilibrium from elements or compounds selected as input. Another module, the *Phase Diagram*, assists users to calculate, plot and edit multicomponent phase diagrams sections.

The following databases were utilized in the present work:(7)

- *FToxid solution database* (FToxid53Soln.sda): contains oxide solutions evaluated and optimized by the FACT group; one of these is the molten slag phase (SLAGA), which contains the fully optimized CaO-SiO_2-CrO-Cr_2O_3-Al_2O_3 system. The molten slag phase is represented accordingly to the modified quasichemical model, which is described in the literature by Pelton and Degterov.(8)
- *FToxid compound database* (FToxid53Base.cdb): contains 247 stoichiometric solid and liquid oxide compounds evaluated and optimized by the FACT group to be thermodynamically consistent with the FToxid solution database. The following compounds were available for the calculations: SiO_2 (tridymite, cristobalite), CaO, $CaSiO_3$ (wollastonite and pseudo-wollastonite), Ca_2SiO_4, Ca_3SiO_5, $Ca_3Si_2O_7$, Cr_2O_3, Cr_3O_4, $CaCr_2O_4$, $(Ca_2Cr_3)Cr_{10}O_{20}$ (phase “X”), $(CaCr)Si_4O_{10}$, $Ca_3Cr_2Si_3O_{12}$ (uvarovite).
- *FACT53* (FS53Base.cdb): contains data for over 4500 compounds (pure substances) and is the updated version of the old FACT general compound database. It contains data from standard compilations as well as most of the data for those compounds which have been evaluated and optimized to be thermodynamically consistent with the FACT FToxid solution database. For the present work only the compounds Cr(s) and O_2 (g) were employed.

The CaO-rich part of the system CaO-CrO-Cr_2O_3-SiO_2 (*i.e.*, compositions in the CaO-Ca_2SiO_4-$CaCr_2O_4$ triangle) in air was not treated in the optimization of FactSage databases.(9)

Caution is needed when selecting phases for participating in the equilibrium state. The application suggests phases that participate in the equilibrium state which should not be there. One example is the phase CrO_2(s) contained in the database FACT53; if this phase is selected among the possibilities for the equilibrium state, the results are inconsistent. Considering the system Cr_2O_3-CrO_2, the last phase exists only in equilibria for pressures higher than atmospheric.(10)

Some problems were experimented with the ‘phase diagram’ module of the used software, they seemed to be related with some equilibrium conditions or chosen phases.

3 THERMODYNAMIC ANALYSIS

The present computational thermodynamic analysis will be restricted to the Cr-Ca-O-Si system. Also, due to industrial relevance, emphasis will be given to the region corresponding approximately to the gray composition tetrahedron limited by CaO-SiO_2-CrO-Cr_2O_3 'compounds', Figure 1.

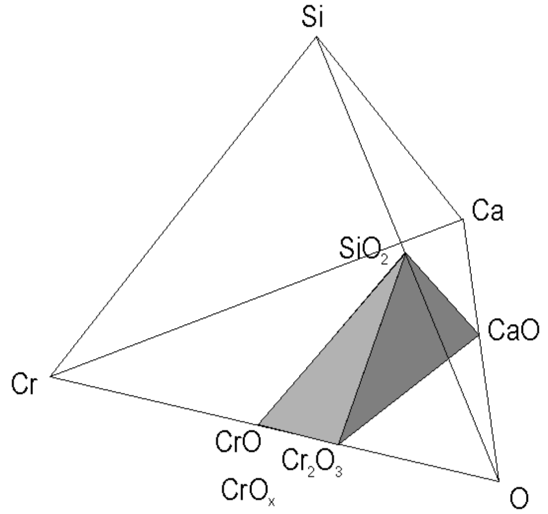

Figure 1: Cr-Ca-O-Si system showing schematically (in gray) the volume composition limits of the present investigation (sub-system CrO-Cr_2O_3-SiO_2-CaO)

3.1 The CrO-Cr_2O_3-CaO System

This system corresponds approximately to the *base* of the gray tetrahedron depicted in Figure 1. The relatively uncomplicated system is of concern for the steel maker for the reason that EAF stainless steel production practice starts with CaO.

The influence of the oxygen pressure on the equilibrium state (actually, the *system* pressure) can be easily seen with the help of this system. Figure 2 (b and d) shows the calculated phase diagrams for the CaO-$CrO_{1.5}$ system at two fixed oxygen pressures, in comparison with diagrams from the literature, Figure 2 (a and c).

If CaO and '$CrO_{1.5}$' are mixed in a proportion given by a point on the abscissa axis and equilibrated with oxygen at the prescribed pressure, then all the equilibrium phases can be read from the diagram.

In spite of the appearance, phase diagrams of Figure 2 are *not* true binary phase diagrams (lever rule does not apply), but instead, they are isobaric lines on the Ca-O-Cr ternary diagram starting at CaO and ending at Cr_2O_3.

The importance of these diagrams is as follows. It is known that an iron-chromium bath at steelmaking temperatures around 1.600ºC will oxidize, giving origin to solid products Cr_2O_3 or $FeO{\cdot}Cr_2O_3$, under oxygen deficient and fairly oxidant conditions, respectively. The addition of CaO to the Cr_2O_3 – which is in equilibrium with a Fe-Cr melt with chromium content higher then the *critical chromium* – can produce two types of effects, as function of the oxygen partial pressure. For low pressure, *e.g.* $pO_2 = 1x10^{-10}$ [atm], the solid phase $CaCr_2O_4$-alpha will form, as predicted by thermodynamic determinations, Figure 2. For more oxidant conditions, however, the *fluxing* effect of lime can be observed and the chances are high of finding a two-phase equilibrium state, with *liquid* oxide in equilibrium with pure solid CaO.(11).

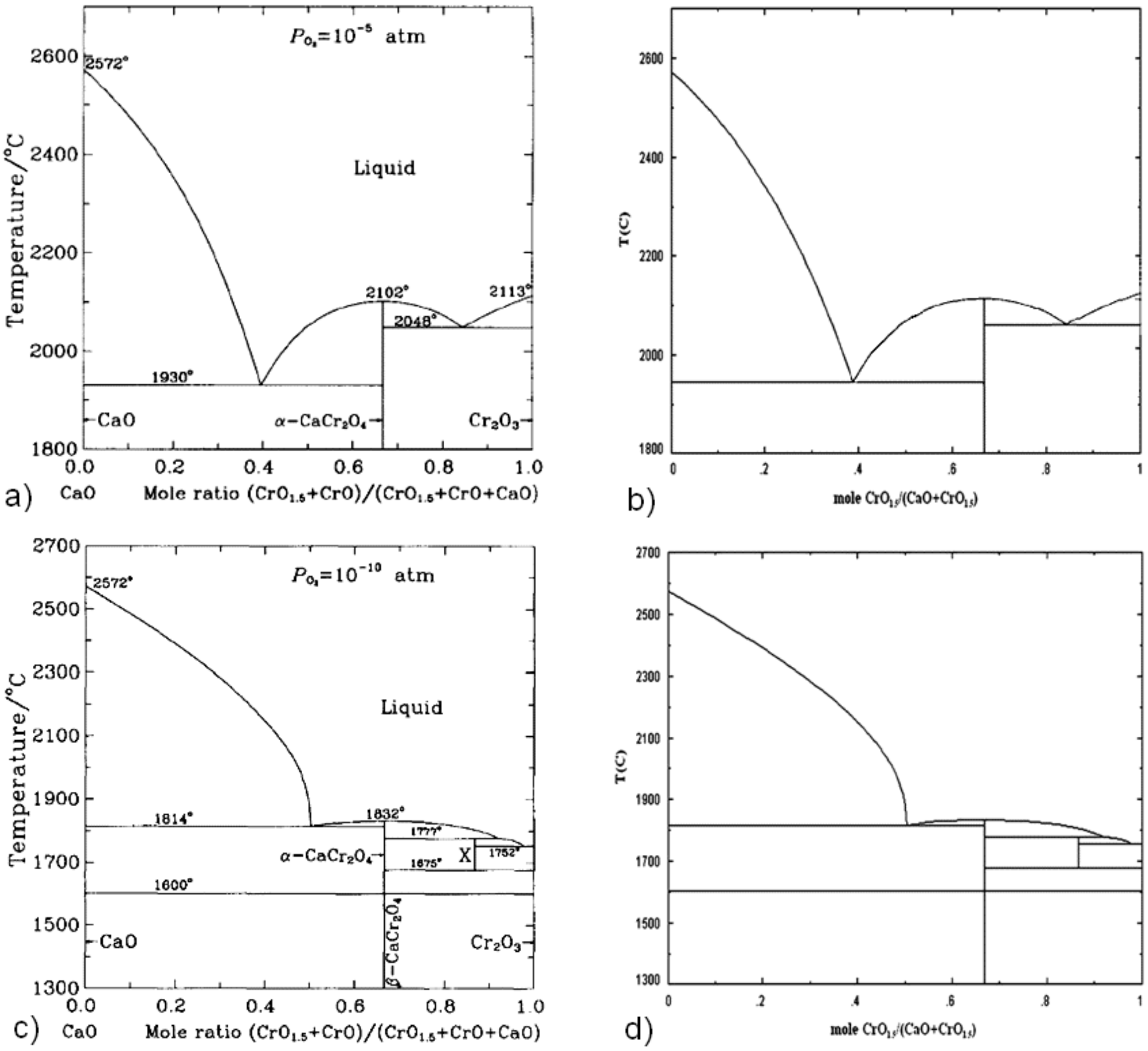

Figure 2. Influence of pressure on phase diagrams; (a) and (b), *pO*$_2$= 1x10^{-5} [atm], (c) and (d), *pO*$_2$= 1x10^{-10} [atm]. Sources: (a) and (c), reference (8); (b) and (d), present work

Solid Cr_2O_3 produced by initial stainless steel scrap fusion, then, could be turned into a liquid phase under such conditions. However, as pointed out previously, since the CaO-rich part of the system in air was not treated by the producer of the thermodynamic database in the data optimization, the determination of the equilibrium state for this condition is not possible.

Nevertheless, for CaO-rich slags, the last situation reflects more properly the top slag layer, while the first one would resemble the conditions for layers depleted in oxygen, nearer to the steel melt.

A second type of diagram can be seen in Figure 3. This Figure is a projection through the Cr-corner of the Cr-Ca-O phase diagram to the CaO-CrO join. That is, if CaO and ‘CrO’ (*e.g.* as a mixture of Cr_2O_3 and chromium) are mixed in a proportion given by a point on the horizontal axis and equilibrated with excess Cr, then the equilibrium phase assemblage can be read from the diagram.

Experimentally, the slag is put in contact with metallic chromium (chromium activity is taken as *unity* for pure Cr). Main feature to be emphasized here is the *variable pressure*; for each point on the axis the system alters its pressure freely in order to reach the equilibrium state. As a result, differently from the previous, this diagram is a *non*-isobaric diagram.

The CaO-based slag layer in contact with the steel melt experiences an analogous situation; main difference to be emphasized here is, in essence, a lower value for chromium *activity*.

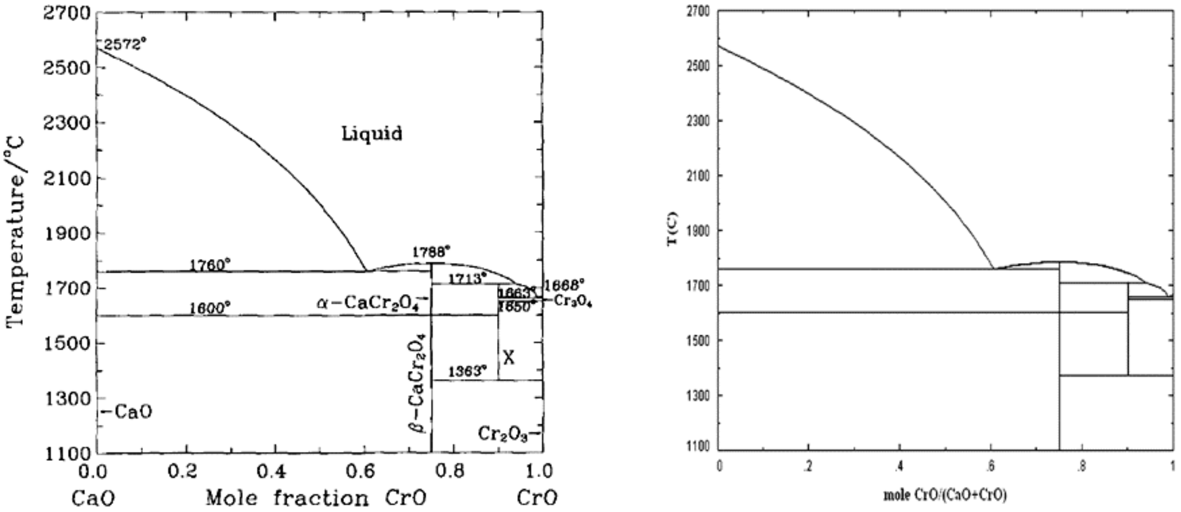

Figure 3. CaO-'CrO' phase diagrams; system in equilibrium with metallic chromium. Sources: left, reference (8); right, present work

3.2 The CrO-Cr2O3-SiO2-CaO System

Existent slags are not as simple as those described by the Cr-Ca-O system. In order to improve the complexity of the slag simulation, it is interesting to introduce the ubiquitous SiO_2. The presence of SiO_2 in the slag is related to the oxidation of the Si in the scrap and to the use of ferroalloys in the manufacture of stainless steels.

Figure 4 shows an isobaric diagram of this system for the total pressure of $1x10^{-10}$ [atm]. If '$CaSiO_3$' and Cr_2O_3 are mixed in a proportion given by a point on the abscissa axis and equilibrated with oxygen at the prescribed pressure, then all the equilibrium phases can be read from the diagram.

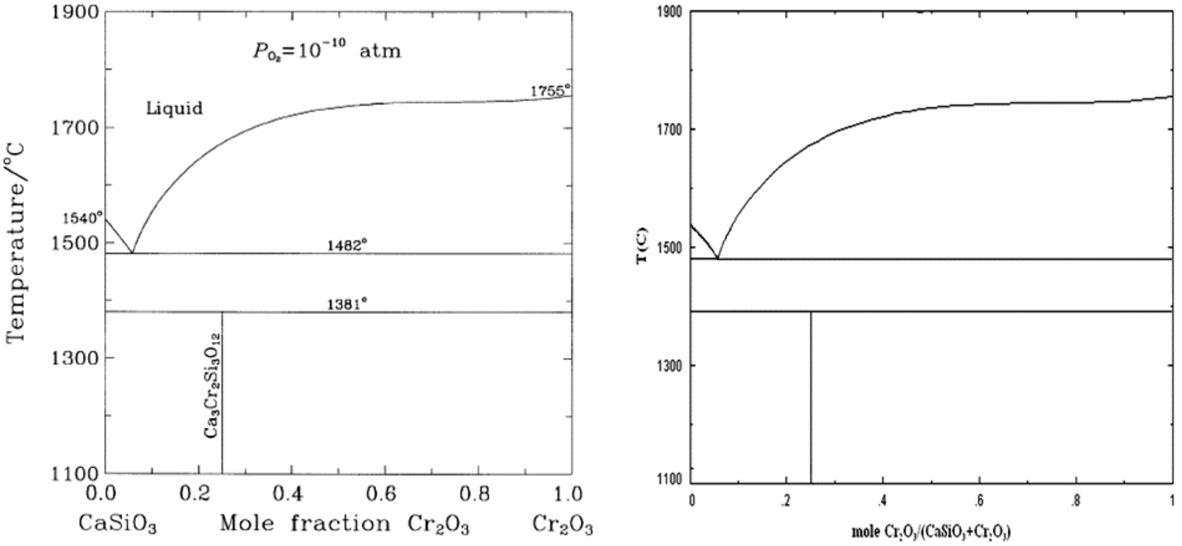

Figure 4. $CaSiO_3$-Cr_2O_3 phase diagrams for oxygen pressure of $1x10^{-10}$ [atm]. Sources: left, reference (9); right, present work

In spite of the appearance, phase diagrams of Figure 4 are, again, *not* true binary phase diagrams. As was the case with the diagrams from previous system, they are made up of isobaric *lines* from the Ca-O-Cr-Si quaternary system, starting at the *composition* '$CaSiO_3$' and ending at phase Cr_2O_3, within the plane Cr-O-$CaSiO_3$, Figure 5.

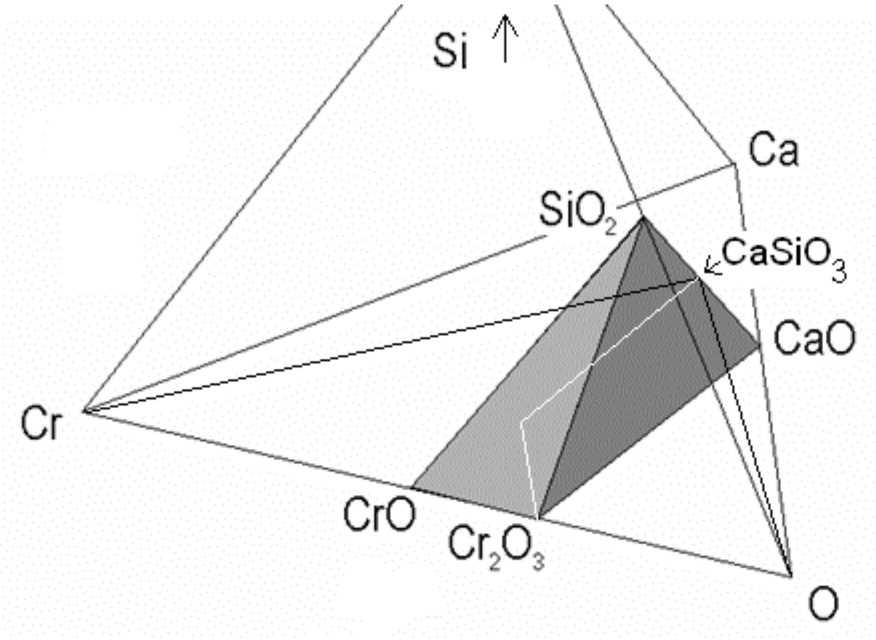

Figure 5. Composition tetrahedron of system Ca-O-Cr-Si showing schematically the plane Cr-O-$CaSiO_3$ (binary molar basicity = 1) and the isobaric (white) line of pressure equal to 1.0×10^{-10} [atm] (within the plane), from the composition '$CaSiO_3$' to the phase Cr_2O_3, at a single temperature (see Figure 6 for comprehension)

Phases at equilibrium state for the Cr-O-$CaSiO_3$ plane were determined for the temperature of 1.600ºC. In order to see the effect of pressure, two pressures (0.21 and 1×10^{-10} [atm]) were chosen. Both pressure values are higher then the Cr-Cr_2O_3 equilibrium pressure (7.6×10^{-13} [atm]). Results can be seen in Figure 6.

The most important field, where Cr_2O_3, atmosphere and liquid slag phases are in equilibrium, can be clearly distinguished. The change in liquid slag *composition*, as a function of the system pressure, is easy to notice; see Figure 6 (insert). This fact explains the possibility of solid Cr_2O_3 precipitation or dissolution by a change in pressure for a fixed *system composition*. White line of Figure 5 can be seen here as the left triangle side plus a vertical line segment.

On the other side, for every *fixed* pressure, an increase in the $CaSiO_3$ mole fraction behind a 'threshold' value will result in the dissolution of solid Cr_2O_3 – the *boundary* mole fraction being set by the system pressure. Taking it in the other way around, for O_2 pressures near that of the atmospheric air, it is clear that Cr_2O_3 saturation happens very easily.

Part of this information can also be seen in diagram of Figure 4, for that pressure. What is not possible to see, both in Figure 4 and 6, are the liquid slag compositions. This will be done later.

When oxygen (system) pressure falls below the Cr_2O_3 equilibrium pressure, *metallic* chromium takes part in the equilibrium state. Tie lines between Cr and slag can be seen in the field at the 'left' side of the liquid slag phase field in Figure 6.

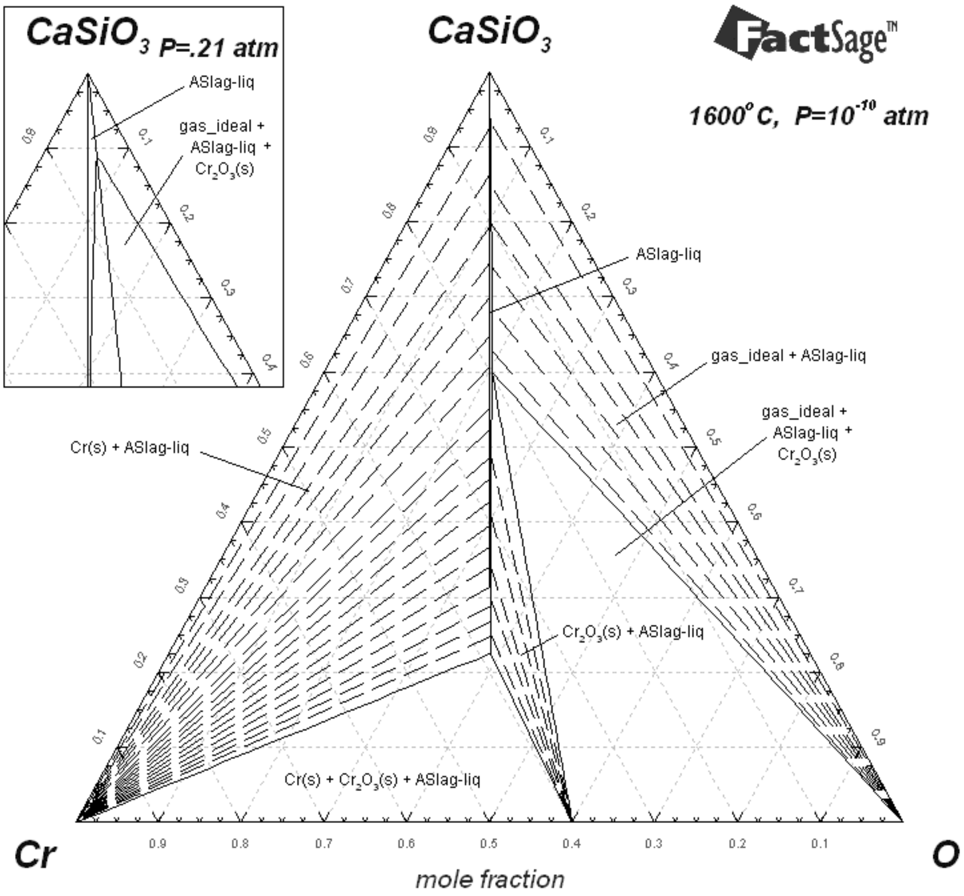

Figure 6. Phase diagram of the system Cr-O-$CaSiO_3$ at two different pressures

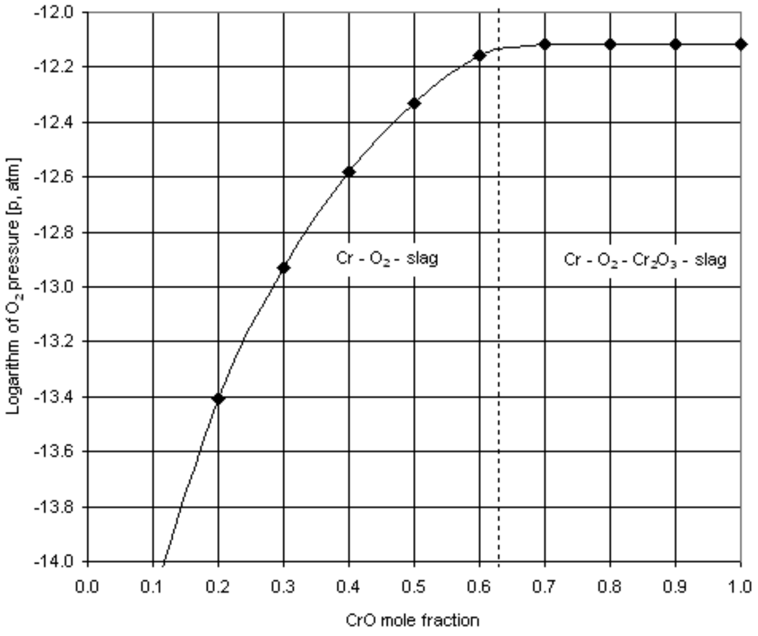

Figure 7. Logarithm of O_2 pressure for the Cr-slag and Cr-Cr_2O_3-slag phase equilibria

Figure 7 shows the logarithm of O_2 pressures for the liquid slag-Cr-atmosphere phase equilibrium. As can be seen, pressure values decrease strongly towards an increment in the $CaSiO_3$ mole fraction, so that an almost 'pure' $CaSiO_3$-

slag in equilibrium with Cr requires a *very* low oxygen pressure. On the opposite direction, at the field of solid Cr_2O_3 in equilibrium with metallic Cr, the pressure is constant and assumes the highest value for this condition.

For a better understanding, liquid slag compositions for three important situations from the Cr-O-$CaSiO_3$ 'section' of the Ca-O-Cr-Si quaternary diagram where determined and can be seen in Table 1.

Table 1. Slag compositions in equilibrium with solid Cr_2O_3, and with metallic Cr, as function of the pressure, binary molar slag basicity is set equal to unity

O_2 pressure [atm]	Phases at equilibrium	Liquid slag composition [%, mole]			
		CaO	SiO_2	CrO*	Cr_2O_3
0.21	Atm., slag, Cr_2O_3	49.4	49.4	0.064	1.18
$1.0x10^{-10}$	Atm., slag, Cr_2O_3	43.1	43.1	13.3	0.48
$7.6x10^{-13}$	Atm., slag, Cr_2O_3, Cr	27.0	27.0	45.7	0.31

*CrO is, here, a slag *constituent*

The interpretation of the results can be as follows: For a position at the top of the slag layer – which can be assumed as beeing in equilibrium with atmospheric air – the liquid slag composition is practically CaO-SiO_2. A point in the 'middle' of the liquid slag layer will show a composition around 13.3% CrO. System pressure must drop to a value of $7.6x10^{-13}$ [atm] in order for a slag layer to be in equilibrium with chromium; for this slag, CrO content is very high, of 45.7%. All values are molar. Relative *amounts* of Cr_2O_3 and slag are, of course, to be taken into consideration.

Morita et al.(12) displayed the influence of the slag basicity for a fixed pressure of $6.95x10^{-11}$ [atm]. Though their diagram are set perpendicularly to the plane Cr-O-$CaSiO_3$ of the present work, the corresponding CrO slag level for chromium oxide saturation shows the same order of magnitude as the value found here.

The information from the last equilibrium line is interesting. The very low pO_2 required for the 'pure' CaO-SiO_2-slag and Cr equilibrium seems to be difficult to establish in the system – more probably, the oxygen level will be higher for the actual conditions of the steelmaking. If it remains below the Cr-Cr_2O_3-Slag equilibrium, as results, the CrO content of slag will be lower then 45.7% – but not nil as well.

4 CONCLUSION

The slags in the Ca-O-Cr-Si quaternary system were studied with the help of metallurgical thermodynamics. From the observed results, for N CaO/N SiO2 = 1, it must be concluded that this systems shows two different kinds of behaviors, depending on the system pressure.

For pressures higher then that of the Cr_2O_3-Cr equilibrium pressure, of $7.6x10^{-13}$ [atm], most of the equilibrium states will show liquid slag in equilibrium with the chromium oxide.

For pressures lower then that, most of the equilibrium states will show chromium in equilibrium with the slag. For some slag compositions, however, the needed oxygen level is very low.

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